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Methyl bromide loss rates in surface waters of the North Atlantic Ocean, Caribbean Sea, and eastern Pacific Ocean (8°–45°N)

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Abstract. The first-order loss rate constant of methyl bromide was measured in surface seawater samples from the North Atlantic Ocean, Caribbean Sea, and coastal eastern Pacific Ocean during May–July 1998. A stable isotope incubation technique was used, which consisted of spiking seawater samples with $^{13}CH_3Br$ and following the loss rate of the isotopically labeled spike with gas chromatography and isotope dilution mass spectrometry. The analysis of both filtered and unfiltered aliquots of seawater provides insight into the relative importance of chemical and particle-related (presumably biological) degradation pathways. Over the entire cruise, first-order total degradation rate constants ranged from 0.03–0.40 day^{-1}. On average, higher rate constants were observed during the last part of the cruise in the Caribbean Sea (mean 0.34 day^{-1}) and coastal Pacific waters (0.31 day^{-1}), than in the earlier passage through the North Atlantic Ocean (0.18 day^{-1}, legs 1 and 3). In the warm waters of the Caribbean Sea and the Pacific, total degradation rate constants were controlled primarily by chemical losses (0.30 and 0.25 day^{-1}, respectively). In the colder Atlantic waters the average chemical loss rate constant was lower (0.11 day^{-1}), and biological losses constituted a significant fraction of the total loss rate constant (35%). Chemical loss rate constants varied strongly with water temperature, in good agreement with previous determinations of the rate constant for methyl bromide removal from seawater due to chloride substitution and hydrolysis. Biological losses were detected in most of the water samples analyzed, suggesting that the biological capability to degrade methyl bromide is ubiquitous in the oceans. Rate constants for biological removal exhibited no apparent relationship to seawater temperature, salinity, chlorophyll, or bacterial counts.

1. Introduction

The oceans play an important but complex role in the global biogeochemical cycle of methyl bromide. Methyl bromide is both produced and destroyed in the surface ocean at rates that significantly impact its tropospheric burden and lifetime [*Butler*, 1994; *Yvon and Butler*, 1996]. Destruction of methyl bromide in the surface ocean has several important consequences. The loss of biogenic methyl bromide produced within the mixed layer limits emissions from this source into the atmosphere. The destruction of methyl bromide in the water column also enhances the removal of atmospheric methyl bromide derived from terrestrial (anthropogenic and biogenic) sources. Because the air/sea flux is proportional to the concentration gradient between surface ocean and atmosphere, the oceans can act as a "buffer" against changes in atmospheric concentrations caused by changing terrestrial emissions or atmospheric reaction rate [*Butler*, 1994].

Methyl bromide is removed from seawater by both chemical and biological mechanisms. Chemically, it is destroyed by substitution of bromine by chloride ion [*Swain and Scott*, 1953; *Zafiriou*, 1975] and by hydrolysis [*Moelwyn-Hughes*, 1938; *Mabey and Mill*, 1978]. The rate constants of these reactions are highly temperature-dependent, and extrapolations based on laboratory measurements yield lifetimes for methyl bromide ranging from 1–2 days in tropical waters to months in polar ocean waters [*Elliott and Rowland*, 1993, 1995; *Jeffers and Wolfe*, 1996]. *King and Saltzman* [1997] developed a stable isotope ($^{13}CH_3Br$) incubation technique for measuring the loss rate of methyl bromide in seawater samples. They demonstrated that in 0.2 μm filtered or autoclaved seawater the loss rate agreed with the chemical rate. In unfiltered, nearshore Florida waters they observed degradation rate constants significantly greater than the chemical rate constant and concluded that biologically mediated loss of methyl bromide occurs in the ocean at environmentally significant rates. On the basis of filtration experiments, *King and Saltzman* [1997] concluded that the process of biological removal is associated with bacterioplankton. They also demonstrated that at least some of the degradation activity in seawater is associated with particles

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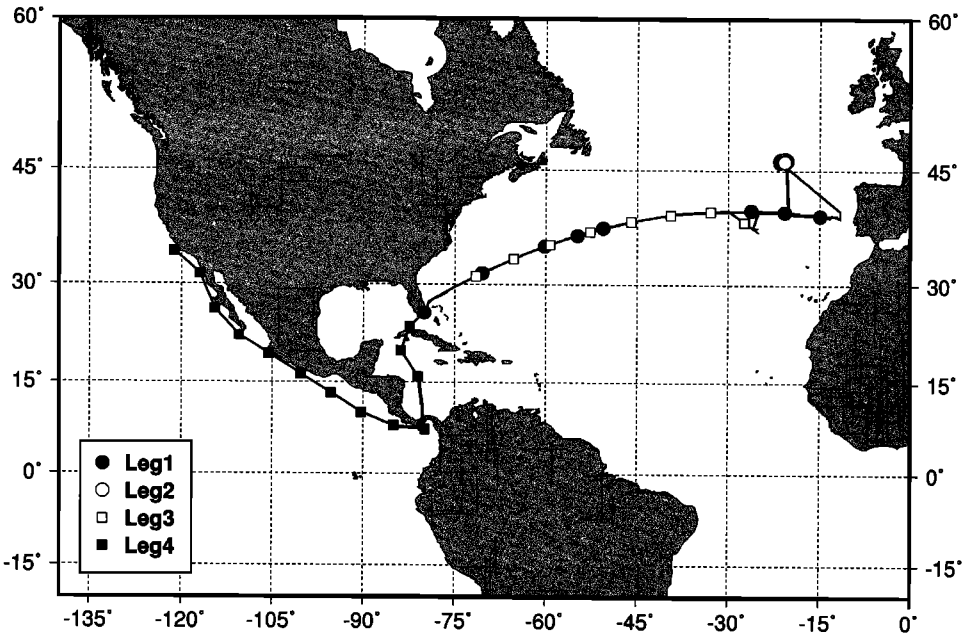

Figure 1. The NOAA ship *Ronald Brown* cruise track during the GASEX-98 experiment (May 8 to July 27, 1998). The dots mark the locations where water samples were collected for this study.

larger than 1 micron, suggesting that some of the bacteria involved may be attached to larger particles or organisms. Global extrapolation of the rate constants observed for biological degradation suggested that biological removal could have a significant impact on the oceanic lifetime of methyl bromide [*King*, 1997; *Yvon-Lewis and Butler*, 1997].

In contrast to chemical degradation, little is known about the biological mechanism(s) by which methyl bromide is destroyed in seawater. Bacterial degradation of methyl bromide has been demonstrated in laboratory studies of methanotrophs [*Goodwin et al.*, 1997; *Oremland et al.*, 1994], ammonia oxidizers [*Keener and Arp*, 1993], and methylotrophs [*Connell et al.*, 1997, 1998; *Scholtz et al.*, 1988; *Hoeft et al.*, 2000] cultured from a variety of natural waters and soils. Relatively few studies have been carried out on the mechanism of methyl bromide degradation in seawater. *Goodwin et al.* [1997, 1998] detected the oxidation of $^{14}CH_3Br$ to $^{14}CO_2$ in coastal California seawater samples and used inhibitor studies to infer that methylotrophs rather than methane or ammonia oxidizers were responsible. Recently, *Hoeft et al.* [2000] cultured methylotrophic organisms from seawater and found evidence for common metabolic pathways for methyl bromide and dimethylsulfide uptake in some, but not all cases. *Harper et al.* [2000] reported evidence of transhalogenation catalyzed by soil-derived bacterial strains. These studies suggest that there is a wide range of organisms and metabolic pathways which could potentially be involved in the bacterial degradation of methyl bromide in the oceans. The relative importance of various types of microbial sinks and overall magnitude and spatial/temporal variability of the oceanic biological sink are not known.

This study represents the first attempt to carry out shipboard measurements using the stable isotope incubation technique to examine the loss rate constants for methyl bromide in coastal and open ocean waters. The goals for this project were to assess the magnitude and spatial variability of total and biological removal rates and to verify current estimates of the chemical loss rate in seawater. The study was conducted aboard the National Oceanographic and Atmospheric Administration (NOAA) ship *Ronald H. Brown* between May 8 and July 27, 1998. The cruise was composed of four parts (Figure 1): (1) a North Atlantic transect from Miami, Florida, to Lisbon, Portugal (May 8–20); (2) several weeks in a North Atlantic eddy north of the Azores, 45.9° to 46.3°N and 20.7° to 21.6°W (May 26 to June 26); (3) a transect from the Azores to Miami, Florida (June 28 to July 8); and (4) a transect from Miami, Florida, through the Caribbean Sea and the Panama Canal, and northward along the Pacific coast to Newport, Oregon (July 12–27).

2. Methods

The methodology used in this study was similar to that of *King and Saltzman* [1997], with modifications in procedures and instrumentation to make it applicable to shipboard use. The experiment consists of adding a stable isotope spike ($^{13}CH_3Br$) to filtered and unfiltered aliquots of a seawater sample. The loss rate of the isotope tracer is followed by gas chromatography-isotope dilution mass spectrometry. A first-order loss rate constant is derived from the observed decrease in concentration with time. No evidence of nonlinear behavior was observed during these studies, in agreement with earlier work which demonstrated that the loss of methyl bromide in seawater is first order in methyl bromide concentration over the range of 25–1250 p*M* [*King and Saltzman*, 1997]. The apparent first-order kinetics observed in this study (Figure 2) suggest that the stable isotope spike itself did not cause the sample to undergo changes in bacterial populations or enzyme activation which affected the rate of methyl bromide degradation during the course of the incubations. This is contrasted with the results of *Goodwin et al.* [1998], who observed induction times of several hours in coastal seawater incubations with spikes of 300 n*M* methyl bromide. The experimental procedure used in this study does not yield a true "tracer" experiment because the stable isotope spike is added at concentrations

considerably above (approximately 100 times) those of natural methyl bromide in seawater. It would be preferable to use spike concentrations at or below ambient levels. It was not possible to achieve this during this study because of limitations imposed by the sensitivity and precision of the methyl bromide analysis and the desire to keep the incubation time as short as possible.

2.1. Sampling and Analysis

During cruise legs 1, 3, and 4, surface water samples were collected with a 20 L plastic bucket between 1000 and 1200 local time (LT). During leg 2, samples were collected with 10 L Niskin bottles from a depth of 5 m at various times of the day. Additional samples were collected during this leg from various depths within the mixed layer. Upon collection, seawater samples were transferred to borosilicate glass syringes (100 or 150 cm^3) without head space, spiked with $^{13}CH_3Br$ to a level of about 400 pM (approximately 40 to 100 times ambient $^{12}CH_3Br$ concentrations), and incubated in a thermostated, circulating water bath. Previous work has demonstrated that loss of methyl bromide from these syringes via volatilization is negligible over the course of 24 hours [*King*, 1997]. The water bath temperature was usually set to the in situ temperature of the seawater sample to be incubated. However, during leg 2, samples were collected at various depths from Niskin bottles mounted on a rosette. Because we used only one incubator, the temperature of the near-surface sample was used for incubation of all the samples from the same cast. The incubation temperature was maintained to within ±1°C. During leg 2 the water column temperature decreased by about 2°C between surface and 100 m and about 4°C between surface and 250 m. The thermocline was typically found between 15–35 m. The extent to which changes in temperature and pressure affect methyl bromide biological degradation rates is not known. Consequently, the degradation rate constants reported in this study for leg 2 samples collected at depth do not necessarily reflect in situ rate constants. Sea surface temperature (SST) and the salinity were measured with a flow-through Seabird Electronics SBE-21 thermosalinograph plumbed to an intake at the ship's bow approximately 5 m below the water line. During leg 2, seawater temperature and salinity were measured using a conductivity-temperature-depth (CTD) profiler (Seabird Electronics 911 Plus) mounted on a rosette. For some seawater samples, additional aliquots were filtered through a 0.2 μm Whatman membrane filter, Anotop 25 Plus (legs 1, 2, 3) and Polycap AS (leg 4), before addition of the $^{13}CH_3Br$ spike. The spike concentration remained far below saturation for methyl bromide, which is estimated to be 0.29 M at 25°C [*De Bruyn and Saltzman*, 1997].

The loss of $^{13}CH_3Br$ from the sample was subsequently monitored at 2 to 4 hour intervals for periods ranging from 8 to 24 hours (10 hours as an average). Because incubation of a seawater sample in a closed container creates a system which, with time, tends to differ from the oceanic environment [*Gieskes et al.*, 1979; *Goldman et al.*, 1981; *Venrick et al.*, 1977], we kept the incubations as short as experimentally feasible. For analysis, about 20 cm^3 of sample was used to flush connecting tubing and fill a 16.5 cm^3 calibrated volume. The calibrated volume was thoroughly purged with ultrahigh-purity helium between samples. The sample was then transferred from the calibrated volume to a glass fritted purge vessel with a stream of helium. The sample was spiked with an internal standard (CD_3Br), and methyl bromide was stripped from the seawater

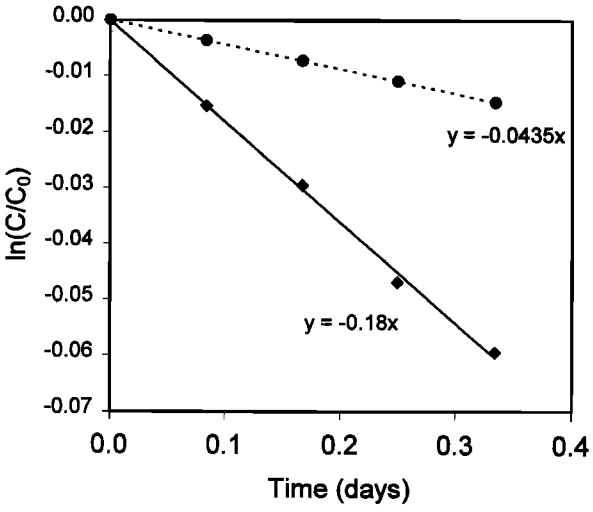

Figure 2. Methyl bromide ($^{13}CH_3Br$) degradation measured on May 19, 1998. The data shown are unfiltered (diamonds) aliquots of a surface seawater sample; circles represent chemical uptake calculated according to equation (1). Data are plotted as natural log of the ratio of the concentration to the initial concentration versus time. The slopes of the linear regression lines represent total (solid) and chemical (dotted) degradation rate constants.

with helium (~80 cm^3 min^{-1} for 12 min). The stripping efficiency for methyl bromide under these conditions is 99%. The gas was dried by passage through $Mg(ClO_4)_2$, and methyl bromide was trapped in a stainless steel tube (20 cm × 0.5 mm ID) packed with Unibeads 1S at −65°C. Desorption was performed at 140°C, and chromatographic separation was achieved using a Chrompack Poraplot-Q capillary column (25 m × 0.25 mm ID, DF 8 μm) held at 110°C for the duration of the run.

Methyl bromide detection was performed with a quadrupole mass spectrometer (HP 5973) with electron impact ionization in selected ion monitoring mode. Masses (m/z) 97 and 99 were monitored for methyl bromide. The signal at m/z 99 was derived entirely from $^{12}CD_3{}^{81}Br$, while the signal at m/z 97 was a combination of $^{13}CH_3{}^{81}Br$ and $^{12}CD_3{}^{79}Br$. The CD_3Br 97/99 ion ratio remained constant during the time of incubation (relative standard deviation equal to 0.2%, n = 5), from which the CD_3Br-97 contribution to the ion-97 signal can be calculated. The ^{13}C fraction of m/z 97, which decreased with time due to the consumption of $^{13}CH_3Br$ during the incubation, was calculated by subtracting the CD_3Br fraction of the m/z 97 signal. Variations in the m/z 99 signal (internal standard) were used to compensate for drift in the detector response, possible variability in purging efficiency between samples, or minor losses in the sample flow path. At the spike concentrations used in this study, the precision of an individual $^{13}CH_3Br$ measurement was ±0.2%.

2.2. Data Analysis

The first-order total loss rate constant k_{total} was determined from the slope of the least squares regression fit to a plot of the natural logarithm of $^{13}CH_3Br$ concentration normalized to the initial concentration against time (Figure 2). On average, 5 to 6 points were used to calculate the slope of the regression line, with 3 and 10 points as lower and upper extremes. The total loss rate constant was then compared with the chemical loss rate constant k_{chem} calculated according to the rate expression

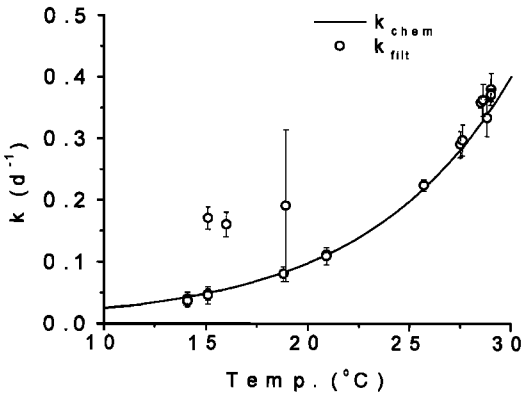

Figure 3. Comparison between measured (k_{filt}) and calculated (k_{chem}) loss rate constants after normalization to salinity 35 and correction for kinetic carbon isotope effect (k_{13C}/k_{12C}). The open circles with the error bars (95% confidence level) represent measured values, and the solid line represents the calculated k_{chem} rate constant from *King and Saltzman* [1997].

given by *King and Saltzman* [1997], shown below (equation (1)). The relative uncertainty in the chemical rate expression is estimated to be ±7% at the 95% confidence interval (D. King, personal communication, 2000). The difference between the total and the chemical degradation rate constants is attributed to biological activity. The uncertainty of each rate constant measurement was estimated at the 95% confidence interval from the variance in the slope of the linear regression [*Natrella*, 1966]. For most samples the uncertainty ranged from 0.01 to 0.03 day^{-1} (5 to 25% of the observed rates), with better relative precision generally associated with faster rates. The loss rate constants reported in this paper typically represent a single incubation of a given water sample.

The measured loss rate constants were corrected for kinetic isotope effects in order to estimate the loss rate constant for natural methyl bromide, which consists primarily of $^{12}CH_3Br$. *King and Saltzman* [1997] measured the ^{13}C kinetic isotope effect associated with the chemical loss of methyl bromide in seawater at 21° and 29°C and obtained a value of $^{12}k/^{13}k$ of 1.074 ± 0.009. No information is currently available regarding the kinetic isotope effect associated with biological uptake of methyl bromide in seawater. In this study, the chemical fractionation factor was applied to all measured rates. This approach may slightly overestimate the biological fractionation. To our knowledge, the largest biological ^{13}C isotope effect observed to date is that accompanying methanogenesis ($^{12}k/^{13}k$ = 1.075 [*Rosenfeld and Silverman*, 1959]), which is similar in magnitude to the chemical fractionation factor used here. Less isotopic fractionation has been observed to be associated with other processes such as methane oxidation (1.016–1.027 [*King et al.*, 1989; *Tyler et al.*, 1994; *Reeburgh et al.*, 1997]) and lactate oxidation (1.00–1.01 [*Kaplan and Rittenberg*, 1964]). If there were no fractionation associated with biological methyl bromide degradation, the rate constants reported in this paper would need to be reduced by 7.4%, which is within the experimental uncertainty of most of the measurements.

3. Results and Discussion

3.1. Filtered Seawater Samples

Methyl bromide loss rate constants were measured in filtered seawater samples during this study to provide a basis for comparing the rate constant for chemical loss in oceanic samples with the chemical rate constants estimated from laboratory experiments. *King and Saltzman* [1997] developed the following empirical expression for the chemical rate constant in seawater, based on an Arrhenius fit to the kinetic data from their study:

$$k_{chem}(day^{-1}) = (5.083 \times 10^{18} e^{-13{,}207/T})[Cl^-] + k_{H_2O}, \quad (1)$$

where T is temperature in K, $[Cl^-]$ is the molar concentration of chloride, and k_{H_2O} is the hydrolysis rate constant (per day) given as a function of temperature by *Moelwyn-Hughes* [1938].

$$k_{H_2O}(day^{-1}) = (8.64 \times 10^4) \times 10^{(112.656 - 10{,}236/T - 34\,259 \log T)}. \quad (2)$$

In order to compare our field measurements to (1) the rates measured on filtered samples were normalized to salinity of 35‰ using the formula

$$k_{filt-35} = (k_{filt} - k_{H_2O}) \frac{[Cl]_{35}}{[Cl]_{filt}} + k_{H_2O}, \quad (3)$$

where $[Cl]_{35}$ is the molar concentration of chloride ion in seawater of salinity 35‰ at the temperature of incubation. $[Cl]_{filt}$ is the molar concentration of chloride ion in the filtered seawater sample at the temperature of incubation. The molar

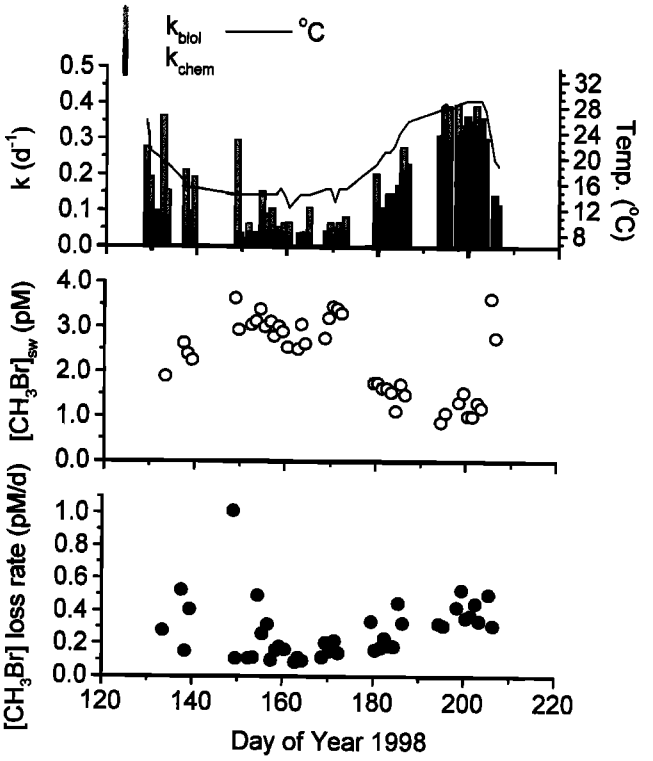

Figure 4. CH_3Br degradation rate constants measured during the GASEX-98 cruise. The black and gray bars represent chemical and biological loss rate constants, respectively. The total height of the stacked bars represent total degradation rate constants. The three major gaps along the time axis (days 139–148, 172–179, and 186–193) separate different legs of the cruise. The solid line is sea surface temperature. (middle) surface ocean CH_3Br concentrations from *King et al.* [2000]. (bottom) CH_3Br loss rates (pM day^{-1}), calculated from the above data (k_{total} $[CH_3Br]$).

concentration of chloride ion in seawater was calculated according to the following expression:

$$[\mathrm{Cl}] = \frac{S\rho(T, S)}{1.80655 \times 35.453}, \quad (4)$$

where S is salinity, $\rho(T, S)$ is density (g cm^{-3}) of seawater derived from the international equation of state [*United Nations Educational, Scientific, and Cultural Organization (UNESCO)*, 1987], 1.80655 is a conversion factor from chlorinity to salinity [*Millero*, 1982], and 35.453 is the atomic weight of chlorine.

Figure 3 is a plot of the methyl bromide loss rate constants from 15 filtered samples. The measurements have been normalized to 35‰ and superimposed on the kinetic expression (equation (1)) for chemical loss in seawater with a salinity of 35‰. The samples cover the temperature range of 14–29°C. The majority of the data agree well with the kinetic expression, taking into account the uncertainty in both the cruise data and the kinetic expression (95% confidence level). Three of the filtered samples had measured loss rate constants that were significantly greater than the calculated loss rate constants at the corresponding temperature. These samples were collected on the first leg of the cruise with the use of 2.5 cm diameter Whatman Anotop 25P, 0.2 μm filters. We speculate that in a few cases of high filter loading, elevated pressure may have caused cells to rupture, releasing intracellular enzymes into the solution. Such enzymes could pass through the filter and enhance the observed degradation rate constants. To avoid similar problems in Caribbean Sea and coastal Pacific waters, the Anotop 25P filter was replaced on leg 4 with a higher-capacity Whatman Polycap 35AS filter. A low, constant pressure difference across the filter was maintained using a 2 m column of sample above the filter. All degradation rate constants of samples filtered using this technique were in good agreement with the predicted "chemistry-only" rate constants.

3.2. Unfiltered Seawater Samples

The observed agreement between the measured filtered rate constants and the calculated chemical rate constants enabled calculation of chemical loss rate constants k_{chem} for the entire set of cruise measurements using equation (1) and the measured temperature and salinity. The biological component of the loss rate constant was calculated by taking the difference between the total loss and chemical loss rate constants for each data point where total degradation rate, temperature, and salinity were measured. Total degradation rate constants were measured in 79 water samples, ranging from 0.03 to 0.40 day^{-1}, with a mean of 0.13 ± 0.11 day^{-1} (1σ) (Figure 4). The average total degradation rate constant was lower in the North Atlantic than in the Caribbean Sea and the coastal eastern Pacific, mainly due to lower water temperatures, which resulted in lower chemical degradation rate constants. In contrast, the biological degradation rate constants in the Atlantic were significantly higher than in the other two regions.

There does not appear to be a simple relationship between the rate constant for biological methyl bromide loss and water temperature (R^2 = 0.25 for legs 1, 3, and 4). In addition, no correlation was observed between biological methyl bromide loss rate constants and particulate organic carbon (R^2 = 0.14), bacterial number (R^2 = 0.14), or chlorophyll content (R^2 = 0.03 (P. Matrai, personal communication, 2000)). The highest biological degradation rate constant (0.29 ± 0.03 day^{-1} was observed on May 12 in relatively warm (19°C) Atlantic waters (36°N–55°W) during leg 1 (Figure 4, day 132). A similar rate constant (0.26 ± 0.04 day^{-1}) was observed on May 28 in significantly cooler (14°C) waters at the beginning of leg 2 (46°N–21.5°W, day 148). The four highest biological degradation rate constants were observed early in the cruise, between May 12 and May 28 (days 132–148). High biological degradation rate constants (0.12 ± 0.02 day^{-1}) were observed on June 3 (day 154) during leg 2 in 14°C water and in warmer (19°C) waters at the beginning of leg 3 (June 28, day 179, Figure 4). In each of these cases, biological loss exceeded chemical loss. The high biological degradation rate constant observed at the beginning of leg 3 (day 179) could be associated with the influence of coastal waters, as the sample was collected in the vicinity of the Azores (38.56°N, 27.34°W). However, the remaining North Atlantic samples with high biological loss rate constants were collected far from coastal influence.

Legs 1 and 3 were nearly identical transects across the North Atlantic, separated by approximately 2 months (May 8–19 and June 28 to July 5, respectively). Chemical degradation rate constants on leg 1 ranged from 0.04 to 0.22 day^{-1} with a mean of 0.09 ± 0.06 day^{-1} (1σ). On leg 3, chemical loss rate constants ranged from 0.08 to 0.22 day^{-1} with a mean of 0.14 ± 0.05 day^{-1}, reflecting the slight warming of surface waters during this period. Biological degradation rate constants, however, decreased during this period, ranging from 0.00 to 0.29 day^{-1} (mean 0.11 ± 0.09 day^{-1}) on leg 1 and from 0.00 to 0.13 day^{-1} (mean 0.04 ± 0.05 day^{-1}) on leg 3. These data suggest that chemical and biological degradation rates do not necessarily covary in a given region.

Leg 2 provided a unique opportunity to study the variability of methyl bromide degradation within a single, evolving water mass. The sampling region was selected using satellite altimeter data, which showed a persistent eddy. The time period was selected in order to reach the eddy at the end of the spring bloom when the delta pCO_2 would be the most negative. A patch of water was tagged by injecting SF_6 and ^3He tracers into the mixed layer. The patch was repeatedly surveyed both horizontally, through continuous underway measurements, and vertically, with depth profiles of SF_6 and ^3He along with pCO_2 and nutrients. We analyzed 51 mixed layer samples during a 1-month period. Most of the samples were collected at a depth of 5 m. Several were collected a few meters above and below the thermocline. For all leg 2 samples the average total degradation rate constant was 0.07 ± 0.04 day^{-1} (n = 51) with the chemical and biological components being almost equal at 0.04 ± 0.004 and 0.03 ± 0.04 day^{-1}, respectively.

The highest total degradation rate constants, up to 0.40 day^{-1}, were observed during the last part of the cruise (July 12–25) in warm Caribbean and Pacific waters (Figure 4, days 193–206). Despite the very high total degradation rate constants, the biological rate constants in Caribbean and Pacific waters were similar (mean 0.04 day^{-1}, standard deviation equal to 0.03 day^{-1}) to biological rate constants observed during legs 2 and 3 in the Atlantic. A significantly greater biological loss rate constant (0.11 day^{-1}) was observed during leg 4 only in coastal waters just after crossing through the Panama Canal (Table 1 and Figure 4, July 16, day 197). The similarity of average biological degradation rates over large areas of Atlantic and Pacific Oceans observed during legs 2, 3, and 4 is striking, especially if compared with the higher biological rate constants observed during leg 1. These results, although lim-

Table 1. Degradation Rate Constants k_{total}, k_{chem}, and k_{biol} of CH_3Br During the GASEX-98 Cruise[a]

Date	UT	Numeric Date	Latitude, °N	Longitude, °W	Depth, m	Incubation Temperature	Salinity	k_{total}, day^{-1}	k_{biol}, day^{-1}	k_{chem}, day^{-1}	$k_{filtered}$, day^{-1}	k_{total} Er(α = 0.05)	$k_{filtered}$ Er(α = 0.05)	Data Points
						Leg 1								
May 8, 1998	1930	128.81	25.7933	−80.0667	4	25.7	36.3	0.278	0.054	0.224	···	0.046	···	4
May 9, 1998	1800	129.75	31.5767	−70.5117	0	20.9	36.5	0.194	0.085	0.109	···	0.022	···	5
May 11, 1998	1500	131.63	35.2900	−60.2167	0	19.9	36.5	0.100	0.006	0.094	···	0.089	···	5
May 12, 1998	1300	132.54	36.7350	−54.8017	0	18.9	36.3	0.365	0.285	0.080	0.198	0.033	0.123	5
May 13, 1998	1100	133.46	37.7683	−50.5583	0	18.9	36.4	0.157	0.077	0.080	···	0.013	···	4
May 17, 1998	1000	137.42	40.0483	−26.2517	0	16.0	35.9	0.214	0.164	0.050	0.165	0.040	0.020	5
May 18, 1998	1000	138.42	39.8867	−20.7683	0	15.1	35.9	0.068	0.024	0.044	0.048	0.010	0.009	5
May 19, 1998	0845	139.36	39.3917	−14.9567	0	15.1	35.9	0.194	0.150	0.044	0.175	0.015	0.018	5
						Leg 2								
May 28, 1998	1920	148.81	45.9000	−21.5050	10	14.1	35.67	0.299	0.262	0.037	···	0.038	···	4
					20	14.1	35.67	0.076	0.039	0.037	···	0.025	···	5
					30	14.1	35.67	0.079	0.042	0.037	···	0.011	···	5
May 29, 1998	1300	149.54	46.0983	−21.5533	5	14.1	35.66	0.039	0.002	0.037	···	0.033	···	3
					20	14.1	35.66	0.038	0.001	0.037	···	0.016	···	4
May 31, 1998	1005	151.42	46.1450	−21.5217	5	14.1	35.68	0.065	0.028	0.037	···	0.015	···	5
					10	14.1	35.68	0.070	0.033	0.037	···	0.015	···	5
					25	14.1	35.68	0.110	0.073	0.037	···	0.012	···	5
June 1, 1998	1055	152.45	46.2250	−21.4500	5	14.1	35.67	0.039	0.002	0.037	0.037	0.015	0.010	4
					30	14.1	35.67	0.039	0.003	0.037	···	0.008	···	5
June 2, 1998	1010	153.42	46.2600	−21.3483	5	14.1	35.67	0.038	0.002	0.037	···	0.009	···	5
					25	14.1	35.67	0.092	0.055	0.037	···	0.011	···	4
					30	14.1	35.67	0.101	0.064	0.037	···	0.015	···	5
June 3, 1998	0836	154.36	46.2900	−21.0717	5	14.1	35.67	0.156	0.119	0.037	···	0.013	···	4
					22	14.1	35.67	0.159	0.122	0.037	···	0.019	···	5
					30	14.1	35.67	0.085	0.048	0.037	···	0.012	···	4
June 4, 1998	0910	155.38	46.2133	−20.8850	5	14.1	35.67	0.092	0.055	0.037	···	0.013	···	4
					60	14.1	35.68	0.038	0.001	0.037	···	0.010	···	5
June 5, 1998	1530	156.65	46.0517	−20.7367	5	14.1	35.65	0.109	0.072	0.037	···	0.008	···	6
					40	14.1	35.68	0.056	0.019	0.037	···	0.008	···	6
June 6, 1998	0830	157.35	46.0050	−21.0000	5	14.1	35.66	0.038	0.001	0.037	···	0.011	···	5
					25	14.1	35.67	0.055	0.018	0.037	···	0.010	···	5
					50	14.1	35.70	0.085	0.048	0.037	···	0.009	···	6
June 7, 1998	1015	158.43	46.0033	−21.0283	5	14.1	35.68	0.056	0.013	0.037	···	0.011	···	5
					50	15.1	35.70	0.045	0.002	0.043	···	0.016	···	5
June 8, 1998	0800	159.33	46.0033	−21.0567	5	14.1	35.66	0.067	0.030	0.037	0.040	0.010	0.011	5
					40	14.1	35.69	0.064	0.027	0.037	···	0.008	···	6
June 9, 1998	0835	160.36	46.1100	−20.9900	5	12.2	35.65	0.069	0.042	0.027	···	0.010	···	6
					50	12.2	35.69	0.060	0.033	0.027	···	0.009	···	6
					80	12.2	35.69	0.058	0.031	0.027	···	0.009	···	5
					100	12.2	35.69	0.056	0.029	0.027	···	0.008	···	5
June 11, 1998	1655	162.70	46.2533	−20.9933	5	14.1	35.67	0.038	0.001	0.037	···	0.010	···	5
June 12, 1998	1020	163.43	46.3333	−20.6833	6	14.1	35.76	0.040	0.003	0.037	0.035	0.008	0.007	6
June 13, 1998	0530	164.23	46.1917	−20.4117	5	14.1	35.69	0.039	0.002	0.037	···	0.008	···	6
	1400	164.58	46.1217	−20.4350	5	14.1	35.68	0.072	0.035	0.037	···	0.009	···	6
	2000	164.83	46.0883	−20.3783	5	14.1	35.69	0.111	0.074	0.037	···	0.019	···	6
	0530	164.23	46.1917	−20.4117	40	14.1	35.69	0.038	0.002	0.037	···	0.018	···	4
	1400	164.58	46.1217	−20.4350	40	14.1	35.68	0.040	0.003	0.037	···	0.009	···	6
	2000	164.83	46.0883	−20.3783	40	14.1	35.69	0.047	0.010	0.037	···	0.009	···	5
June 17, 1998	1530	168.65	45.9800	−20.5750	6	15.1	35.67	0.045	0.002	0.043	···	0.006	···	10
June 18, 1998	1015	169.43	45.9767	−20.5767	5	15.1	35.65	0.069	0.025	0.043	0.046	0.013	0.014	5
June 19, 1998	0930	170.40	45.9833	−20.6400	7	13.1	35.65	0.048	0.017	0.031	···	0.008	···	5
					40	13.1	35.67	0.032	0.001	0.031	···	0.008	···	6
June 20, 1998	0740	171.32	45.9900	−20.6233	5	15.1	35.6	0.068	0.023	0.045	···	0.008	···	7
					250	15.1	35.7	0.057	0.014	0.043	···	0.011	···	6
June 21, 1998	0630	172.27	45.9600	−20.7750	5	15.1	35.67	0.046	0.003	0.043	···	0.005	···	7
	0940	172.40	45.9417	−20.8150	5	15.1	35.67	0.045	0.002	0.043	···	0.007	···	5
	1230	172.52	45.9817	−20.8500	5	15.1	35.67	0.065	0.022	0.043	···	0.009	···	4
	1510	172.63	46.0300	−20.8333	5	15.1	35.67	0.064	0.020	0.043	···	0.007	···	5
	1800	172.75	46.0300	−20.7850	5	15.1	35.67	0.063	0.020	0.043	···	0.007	···	7
	2130	172.90	46.0150	−20.7367	5	15.1	35.68	0.085	0.042	0.043	···	0.008	···	6
						Leg 3								
June 28, 1998	1300	179.54	38.5583	−27.3350	0	18.9	36.1	0.205	0.125	0.080	···	0.018	···	6
June 29, 1998	1000	180.42	39.9250	−32.9250	0	19.9	36.0	0.097	0.005	0.093	···	0.008	···	5
June 30, 1998	1000	181.42	39.4550	−39.4617	0	20.9	36.0	0.113	0.005	0.108	0.115	0.010	0.008	6
July 1, 1998	1100	182.46	38.5917	−45.9983	0	20.9	36.0	0.152	0.044	0.108	0.112	0.018	0.014	4
July 2, 1998	1100	183.46	37.2517	−52.7117	0	21.8	36.3	0.130	0.006	0.125	···	0.017	···	5

(*Continued on next page*)

Table 1. (continued)

Date	UT	Numeric Date	Latitude, °N	Longitude, °W	Depth, m	Incubation Temperature	Salinity	k_{total}, day^{-1}	k_{biol}, day^{-1}	k_{chem}, day^{-1}	$k_{filtered}$, day^{-1}	k_{total} Er(α = 0.05)	$k_{filtered}$ Er(α = 0.05)	Data Points
July 3, 1998	1200	184.50	35.5550	−59.2817	0	23.7	36.3	0.175	0.008	0.166	···	0.015	···	5
July 4, 1998	1200	185.50	33.5833	−65.3517	0	24.7	36.4	0.279	0.086	0.193	···	0.021	···	4
July 5, 1998	1200	186.50	31.1467	−71.4983	0	25.7	36.1	0.235	0.017	0.218	0.231	0.016	0.009	4
						Leg 4								
July 12, 1998	1400	193.58	23.7567	−82.3867	0	27.6	36.3	0.315	0.019	0.296	0.309	0.010	0.025	6
July 13, 1998	1400	194.58	20.0000	−83.8733	0	28.6	36.3	0.396	0.053	0.342	0.376	0.022	0.026	5
July 14, 1998	1400	195.58	15.8817	−81.0417	0	27.6	36.4	0.306	0.010	0.296	···	0.018	···	5
July 16, 1998	1400	197.58	7.3800	−79.8617	0	28.5	30.7	0.401	0.109	0.292	0.321	0.013	0.009	5
July 17, 1998	1400	198.58	7.9500	−85.0333	0	28.8	33.0	0.343	0.019	0.324	0.318	0.030	0.030	4
July 18, 1998	1500	199.63	10.1633	−90.3600	0	29.0	33.7	0.368	0.029	0.360	0.360	0.012	0.010	5
July 19, 1998	1500	200.63	13.2600	−95.3767	0	29.0	33.8	0.378	0.038	0.341	0.371	0.016	0.026	6
July 20, 1998	1500	201.63	16.2783	−100.3183	0	29.0	33.6	0.397	0.058	0.339	0.360	0.010	0.009	5
July 21, 1998	1700	202.71	19.4950	−105.6683	0	29.0	34.2	0.363	0.019	0.344	···	0.014	···	5
July 22, 1998	1600	203.67	22.3383	−110.5667	0	27.5	34.6	0.303	0.023	0.280	0.289	0.013	0.021	5
July 24, 1998	1600	205.71	31.4083	−116.9617	0	19.7	33.7	0.148	0.063	0.085	···	0.034	···	3
July 25, 1998	1700	206.71	34.5850	−121.1733	0	18.8	33.2	0.121	0.048	0.073	0.077	0.013	0.012	5

[a]See text for details.

ited, suggest that in open ocean waters the seasonal variability in biological degradation rates may be larger than spatial variability. Additional field measurements will be needed in order to assess the magnitude of seasonal variability.

3.3. Methyl Bromide Loss Rates

The loss rate of methyl bromide (pM day^{-1}) is the product of the total loss rate constant and the methyl bromide concentration (k_{total} [CH_3Br]). Surface water concentrations of methyl bromide during the cruise ranged from 1–4 pM [*King et al.*, 2000] (Figure 4). The surface concentrations exhibit temperature dependence, with lower concentrations in warmer tropical waters and higher concentrations in cooler, temperate waters. As a result, the surface concentrations and total loss rate constants are inversely related (r^2 = 0.5). Hence the calculated loss rate exhibits less variability that either of the other parameters. In warmer waters the loss rates are sufficiently rapid that water column methyl bromide must be controlled largely by water column processes; that is, the rate of exchange of methyl bromide across the air/sea interface is not sufficiently rapid to sustain the observed loss rate. As shown by *King et al.* [2000], those waters are largely undersaturated with respect to the atmosphere. In the cooler North Atlantic waters encountered during leg 2, the low loss rates were associated with high concentrations and supersaturated conditions. Process modeling of these results will be the focus of a subsequent paper (S. A. Yvon-Lewis et al., manuscript in preparation, 2001). Undersaturated conditions have been observed at higher latitudes in both hemispheres [*Moore and Webb*, 1996; *Lobert et al.*, 1997] in colder waters where chemical loss rates are negligible. Measurements of the type presented here are needed for those regions in order to assess whether biological removal of methyl bromide uptake is responsible for undersaturation.

3.4. Time Series Experiments

Two time series experiments were performed on June 13 and June 21 during leg 2 (Table 1), in order to examine the possibility of diel variability in biological loss rate constants. The ship returned every 2 hours to a drifting buoy marking the center of the patch. Seawater salinity and temperature remained constant within 0.01‰ and 0.1°C during the first experiment and within 0.01‰ and 0.4°C during the second. During the June 13 experiment, three sets of samples were collected at 5 and 40 m over 15 hours and incubated at 14.1°C. During the June 21 experiment, six samples were collected over 16 hours at 5 m depth and incubated at 15.1°C. Both experiments show an increase in biological degradation rate constant from the morning toward the evening hours (Figure 5). Biological degradation became detectable about noon, with significantly higher rate constants in the samples collected near sunset. However, because no samples were collected overnight, it is not possible to say at what time the loss rate maximized. The observed trends are significant at the 95% confidence level. The effect is much stronger in surface water (5 m depth), than in the sample taken from 40 m (Table 1), which suggests that the process may be light-related, either directly or indirectly as a result of some other diurnal change in biological activity. Because most of the samples taken in this study were collected during the morning, a diurnal effect could cause a bias in our results. Clearly, more diurnal observations are needed in order to investigate the full extent of this apparent diurnal variability and its impact on oceanic degradation rates.

3.5. Comparison With Previous Work

The only previous measurements of biological methyl bromide degradation rates in seawater are those of *King and Saltzman* [1997] and *Goodwin et al.* [1998]. The rates reported by *King and Saltzman* [1997] are directly comparable to this study in terms of methodology. They reported biological degradation rate constants in 12 coastal seawater samples collected near Miami between December 28 and August 4. Their rates averaged 0.10 ± 0.04 day^{-1}. During this cruise, three samples were collected in close proximity to land. They were collected at the edge of the Gulf Stream near Miami (May 8), near Azores (June 28), and near Pacific entrance to the Panama Canal (July 16). Biological degradation rate constants in these samples were 0.05, 0.13, and 0.11 day^{-1}, respectively, yielding an average rate constant (0.10 ± 0.04 day^{-1}) which is

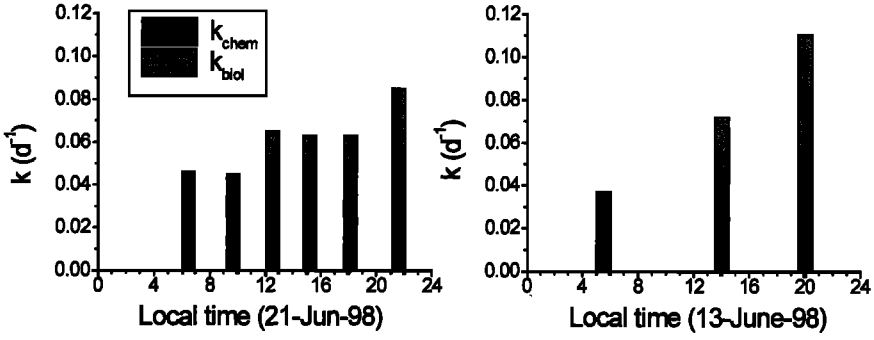

Figure 5. Temporal variations in degradation rate constants for CH_3Br observed at 5 m during two diel experiments inside a tracer-labeled eddy in the North Atlantic during leg 2. The black and gray bars represent chemical (calculated) and biological loss rate constants, respectively. The horizontal axis is scaled in hours (local time). In both cases, biological rate constants appear smaller earlier in the day and larger in evening samples.

not statistically different to that from the Miami measurements.

Goodwin et al. [1998] reported apparent methyl bromide oxidation rate constants for some California coastal seawater samples. The methodology employed in that study was to incubate samples with $^{14}CH_3Br$, and detect oxidation by measuring ^{14}C activity in a carbonate precipitate. This technique detected both the formation of $^{14}CO_2$ and the incorporation of the ^{14}C label into cellular material or other particulates. They reported rate constants 0.003 ± 0.0019 day^{-1} ($n = 5$). Those results are at the low end of the rate constants measured during this study, and considerably lower than nearshore measurements from both this study and *King and Saltzman* [1997]. *Goodwin et al.* [1998] carried out incubations at spike concentrations approximately 10^3-fold greater than those used in this study, and induction periods (i.e., delay prior to the onset of oxidation) of approximately 10 hours were observed. *Goodwin et al.* [1998] inferred that enzyme induction or cell growth may have increased the apparent rate constants and suggested that their reported values should be considered upper limits. The stable isotope incubation technique used in this study and by *King and Saltzman* [1997] detects methyl bromide degradation via all mechanisms, while the ^{14}C technique as used by *Goodwin et al.* [1998] measures only oxidation and incorporation of the label into particulates. If the stable isotope technique yields consistently higher estimates of the loss rate constant, it could indicate that a nonoxidative mechanism, such as transhalogenation to CH_3Cl [*Harper et al.*, 2000], accounts for a significant component of the biological methyl bromide degradation in seawater. A direct comparison of the two techniques on the same water samples would be needed in order to investigate this possibility.

4. Conclusions

This study demonstrates that the stable isotope technique can be applied with sufficient precision aboard ship to measure oceanic degradation rate constants for methyl bromide. The results show that filtered seawater loss rate constants agree well with laboratory-derived rate constants for chloride substitution and hydrolysis. Degradation associated with filterable particulates was detected in most samples, suggesting that biological (presumably bacterial) metabolism of methyl bromide is widespread in the oceans at rates which are environmentally significant. These losses constitute a significant component of the total methyl bromide loss rate constant and should be included in global budget calculations. The diurnal variability observed suggests that light-mediated processes may play a role in methyl bromide degradation. Further field measurements are needed in order to characterize the variability of oceanic methyl bromide loss on a regional and seasonal basis and to investigate the environmental factors and biological mechanisms involved.

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